KEMENTERIAN PENDIDIKAN MALAYSIA

FINAL REPORT
FUNDAMENTAL RESEARCH GRANT SCHEME (FRGS)

Laporan Akhir Skim Geran Penyelidikan Fundamental (FRGS)
Pindaan 1/2015

A **RESEARCH TITLE:** Nanoalloy platinum infiltrated BSCF cathode for enhancement of intermediate temperature solid oxide fuel cell

PHASE & YEAR: 1/2012

START DATE: 1 June 2012
END DATE: 31 May 2014
EXTENSION PERIOD (DATE): RMC LEVEL: 1 June 2014 to 31 December 2014
KPM LEVEL: 1 June 2014 to 31 May 2015 and 1 Jan 2015 to 30 June 2015

PROJECT LEADER: Prof Dr. Sulaiman Ab Ghani
I/C / PASSPORT NUMBER: 520807-04-5269

PROJECT MEMBERS: 1. Prof Dr. Norita Mohamed
(including GRA) 2. Prof Dr. Azizan Aziz

PROJECT ACHIEVEMENT *(Prestasi Projek)*

B

ACHIEVEMENT PERCENTAGE			
Project progress according to milestones achieved up to this period	**0 - 50%**	**51 - 75%**	**76 - 100%**
Percentage (please state #%)			80%

RESEARCH OUTPUT		
Number of articles/ manuscripts/ books *(Please attach the First Page of Publication)*	**Indexed Journal**	***Non-Indexed Journal***
	1	1
Conference Proceeding *(Please attach the First Page of Publication)*	**International**	***National***
		2
Intellectual Property *(Please specify)*		

HUMAN CAPITAL DEVELOPMENT

Human Capital	Number				Others (please specify)
	On-going		Graduated		
Citizen	Malaysian	Non Malaysian	Malaysian	Non Malaysian	
No. PHD STUDENT		1	1		
Student Fullname: IC / Passport No: Student ID:		Mohd Madjid Torkaman E15983532 P-KD0015/10(R)	Farhanini Yusoff 851122-03-5080 P-KD0022/09(R)		
No. MASTER STUDENT					
Student Fullname: IC / Passport No: Student ID:					
No. UNDERGRADUATE STUDENT					
Student Fullname: IC / Passport No: Student ID:					
Total		1	1		

EXPENDITURE *(Perbelanjaan) as Borang K1(RMC)*

C

Budget Approved *(Peruntukan diluluskan)* : **RM**103,000.00
Amount Spent *(Jumlah Perbelanjaan)* : **RM** 81,018.70

Balance *(Baki)* : **RM** 21,981.30
Percentage of Amount Spent *(Peratusan Belanja)* : 78.65%

ADDITIONAL RESEARCH ACTIVITIES THAT CONTRIBUTE TOWARDS DEVELOPING SOFT AND HARD SKILLS
(Aktiviti Penyelidikan Sampingan yang menyumbang kepada pembangunan kemahiran insaniah)

International

Activity	Date (Month, Year)	Organizer
(e.g : Course/ Seminar/ Symposium/ Conference/ Workshop/ Site Visit)		

National

Activity	Date (Month, Year)	Organizer
(e.g : Course/ Seminar/ Symposium/ Conference/ Workshop/ Site Visit)	**4th International Conference for Young Chemists (ICYC) 2013, Bayview Hotel, Georgetown, Penang, Malaysia,** January 30th – February 1st, 2013. Development of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ Modified Glassy Carbon Cathode as Intermediate Temperature Solid Oxide Fuel Cell - Synthesis and Characterization. MAT 03, p135	Universiti Sains Malaysia

	Joint Seminar USM-Nagaoka University of Technology Research Collaboration, Perpustakaan Hamzah Sendut, USM, Penang, Malaysia, October 21st – 22nd, 2013. BSCF-MWCNT Composite Paste Electrode as a Prospective Oxygen Reduction Cathode in a Fuel Cell. p O4	Universiti Sains Malaysia

E PROBLEMS / CONSTRAINTS IF ANY *(Masalah/ Kekangan sekiranya ada)*

Time constraints in synthesising the SOFC.

RECOMMENDATION *(Cadangan Penambahbaikan)*

The extension period requested should be considered.

G RESEARCH ABSTRACT – Not More Than 200 Words *(Abstrak Penyelidikan – Tidak Melebihi 200 patah perkataan)*

A new $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) based composites electrodes for electroreduction of oxygen was developed. The synthesis of pure BSCF using citrate-EDTA complexing method was carried out at different pHs of which pH 9 was the best. The BSCF-MWCNT composites electrode was prepared as pastes and modified glassy carbon electrodes (GCE) by chemical deposition and in situ mechanical mixing. In the pastes type the inclusion and the uniform dispersal of MWCNT within BSCF were confirmed by XRD and SEM studies. The N_2 isotherm study indicated that the surface area of composite paste electrode with specific pore characteristics has improved the BSCF alone electrode by quadruple. The electrochemical impedance spectroscopy (EIS) and cyclic voltammetry demonstrated that the higher ratio of MWCNT was critical in improving the electronic conductivity and kinetics. The BSCF-MWCNT/GCE prepared by chemical deposition had its rate constant improved 1000 times. However, the BSCF-MWCNT/GCE prepared by in-situ mechanical mixing the rate constant was dependent on the MWCNT loading. The Cyclic and hydrodynamic voltammetries of these electrodes in 0.1 M KOH suggested that reduction mechanism followed 4 electron processes. The high electrocatalytic properties maybe useful as a material for oxygen reduction.

Date : 26 July 2015
Tarikh

Project Leader's Signature:
Tandatangan Ketua Projek

H	**COMMENTS, IF ANY/ ENDORSEMENT BY RESEARCH MANAGEMENT CENTER (RMC)** *(Komen, sekiranya ada/ Pengesahan oleh Pusat Pengurusan Penyelidikan)*

Tunggu co utk bentang.

Name:
Nama:

PROF. DR LEE KEAT TEONG
Pengarah
Pejabat Pengurusan & Kreativiti Penyelidikan
Universiti Sains Malaysia

Signature:
Tandatangan:

Date:
Tarikh:

18/8/15

UNIVERSITI SAINS MALAYSIA

長岡技術科学大学
Nagaoka University of Technology

JOINT SEMINAR

Joint Seminar for USM - Nagaoka University of Technology Research Collaboration

October 21st- 22nd, 2013

Bilik Alamanda,
Perpustakaan Hamzah Sendut (PHS II)
Universiti Sains Malaysia
Penang, Malaysia

BSCF-MWCNT composite paste electrode as a prospective oxygen reduction cathode in a fuel cell

Farhanini Yusoff[a], Norita Mohamed[a], Azizan Aziz[b] and Sulaiman Ab Ghani[a]

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Abstract

A composite cathode based on $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) and multiwalled carbon nanotube (MWCNT) was developed. The BSCF has, initially, been prepared by sol-gel method. The composites were prepared by direct mixing of BSCF: MWCNT at 90:10, 80:20 and 70:30 (% w/w). Each mixture as paste was packed into the Teflon® tube before characterization by XRD, SEM, EIS and cyclic voltammetry. The XRD confirmed the inclusion of MWCNT in BSCF. The SEM showed a uniformly dispersed MWCNT within the BSCF. The EIS and cyclic voltammetry showed the higher ratio MWCNT cathode was significant in enhancing the conductivity and kinetics. The cathode was also found to have increased the electro catalysis of oxygen in 1 M KOH (pH 12.0). The voltammetric studies on the oxygen reduction reaction suggested that the incorporation of MWCNT was vital in order to improve the cathode properties in the future fuel cell.

Keywords: BSCF, Catalysis, Cathodes, Composites, MWCNT

MAT-03

DEVELOPMENT OF $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ MODIFIED GLASSY CARBON CATHODE AS INTERMEDIATE TEMPERATURE SOLID OXIDE FUEL CELL-SYNTHESIS AND CHARACTERIZATION

Farhanini Yusoff[1], Azizan Aziz[2], Norita Mohamed[1], and Sulaiman Ab Ghani[1]

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This study reported on the synthesis and characteristic of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) as cathodes of intermediate temperature solid oxide fuel cells. The BSCF were prepared by the EDTA-citrate method with the required molar ratio of EDTA, nitrates salts and citric acid and at experimental pH 5, pH 7 and pH 9. Ammonium hydroxide solution was used as pH adjustor to solutions. The solutions were evaporated yielding the metal-citrate-nitrate gel complex precursors which were then calcined at 900 °C for 5 hours to produce the BSCF powder. The X-ray diffraction showed the powder had pure crystallinity. It was found that the pH value was crucial for chelation process as well as purity of phase obtained. TEM images showed that the particle size was in the range of 50–200 nm. The TGA result revealed that the weight loss was due to the magnitude of oxygen-release of the BSCF structure. The BSCF at pH 9 (BASF9) with the most well-crystallized structure, the largest surface area was the best product and studied further. The BSCF9 solutions at various volumes were deposited on glassy carbon electrode (GCE) and were characterized electrochemically. Cyclic voltammograms showed that the volumes of BSCF used affected the electron transfer, mass transport and capacitive behavior of the modified GCE. The impedance studies have indicated that the electrode process was favorable.

Keywords: $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF), citrate-EDTA, porous material, cathode, BSCF-modified glassy carbon electrode

MAT-04

TETRAMETHYLGUANIDINE-SILICA NANOPARTICLES AS AN EFFICIENT AND REUSABLE CATALYST FOR THE SYNTHESIS OF CYCLIC PROPYLENE CARBONATE FROM CARBON DIOXIDE AND PROPYLENE OXIDE

Muazu Samaila Batagarawa[1] and Farook Adam[2]

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Tetramethylguanidine covalently bonded to silica is reported as an efficient and recyclable catalyst for the synthesis of propylene carbonate (PC) from propylene oxide (PO) and carbon dioxide. The catalyst was prepared, first by the coupling of 3-(chloropropyl) triethoxy silane with silica from Rice husk ash (RHA), to form 3-chloro propyl silica (RHACCl). This was later grafted with tetramethylguanidine molecule to form solid base catalyst (RHAPrTMG). The surface morphology analysis of the catalyst by TEM, revealed the presence of spherical nanoparticles with average particle size of 19.62 nm. In order to prove the successful incorporation of the TMG moiety on the silica surface, the ^{13}C solid state NMR indicated the presence of all the 5 set of carbon atoms in the structure. The effect of various reaction parameters on the catalytic performance were investigated in detail. Under optimised reaction conditions (130 °C, 5.0 MPa, 8 h), over 92 % conversion was achieved, with propylene carbonate selectivity of *ca.* 98 %. The catalyst can be easily recovered by filtration and reused for at least four times without appreciable loss of its catalytic activity. Based on the experimental results, a plausible reaction mechanism has been proposed.

Keywords: Tetramethylguanidine, silica-guanidine nanoparticles, carbon dioxide, propylene oxide, propylene carbonate

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Synthesis and Characterizations of BSCF at Different pH as Future Cathode Materials for Fuel Cell

Farhanini Yusoff[1], *Azizan Aziz*[2], *Norita Mohamed*[1], *Sulaiman Ab Ghani*[1*]

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Received: 22 April 2013 / *Accepted:* 3 July 2013 / *Published:* 1 August 2013

The synthesis of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) using citrate-EDTA complexing method was carried out at pH 5, 7 and 9. Their suitability as cathode materials for intermediate temperature solid oxide fuel cells (SOFC) was investigated. The BSCF solutions was heated to 100 °C yielding a metal-citrate-nitrate gel complex precursor which was later calcined at 1000 °C for a period of 4 hours to produce the BSCF powder. The X-ray diffraction pattern of the calcined powder showed that it had undergone a complete phase formation. It was found that the pH value was crucial for the chelation process as well as for the purity of the phase obtained. The BSCF with a compact particle arrangement was obtained at pH 9. The nitrogen adsorption studies indicated that the BSCF powders had a mixture of microporous and mesoporous particles. Analysis by thermogravimetry revealed that the weight loss resulted from the oxygen-releasing capacity of the BSCF structure. The largest surface area was observed for BSCF powders prepared at pH 9. The BSCF at pH 9 prepared at various solution volumes was deposited on a glassy carbon electrode and characterized electrochemically. Cyclic voltammograms showed that the amount of BSCF deposited influenced the electron transfer, mass transport and capacitance behavior. Electrochemical impedance spectroscopy indicated that the electrode process was favorable.

Keywords: Adsorption; BSCF; Modified electrode; pH; Porosity

1. INTRODUCTION

Mixed ionic-electronic conductors with a perovskite oxide structure are popular materials of choice for solid oxide fuel cell (SOFC) cathodes, catalysts, and also as oxygen permeable membrane [1-3]. One such perovskite is $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) which has attracted great interest among researchers owing to its ultrahigh oxygen permeability and favorable structural stability [4].

A higher BSCF volume means a higher surface area exposed for the reaction thus increasing the capacitance. The capacitance value is linear to a given potential window. From the CV results (data is not shown) the increase in amount will increase the potential window. Therefore, the largest area of potential window in 5 μL of BSCF solution give the largest capacity compared to other volume. Fig. 9 shows the variation of calculated specific capacitance (F/g) versus the different scan rate. These results show that the efficiency of BSCF 5 μL is at its highest. This result also supports the EIS data obtained.

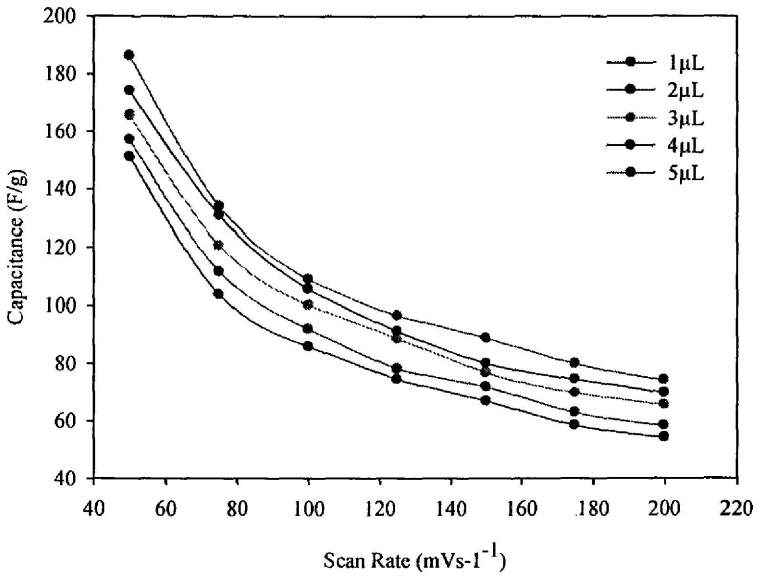

Figure 9. Plot of capacitance *vs.* scan rate for different volumes of BSCF solution

4. CONCLUSION

The effect of solution pH is an important parameter for controlling the BSCF oxides powder characteristics synthesized by the EDTA–citrate method. The BSCF at pH 9 with 5 μL volume is the optimum condition for better material characteristics. The phase formation behavior of BSCF is a complex process and different in every pH tested. Morphology studies show that the particle properties are mostly coarse and agglomerate. A good theoretical correlation between pore sizes, volumes and surface area is obtained. The BSCF oxides are capable of releasing oxygen at 400 °C. The BSCF cathode displays diffusion controlled electrode process. Facile electron transfer is observed when high amounts of BCSF are used as an electrode.

ACKNOWLEDGMENT

This work was supported by the Ministry of Higher Education (MOHE) Fundamental Research Grant Scheme (FRGS) 203/PKIMIA/6711263 and Universiti Sains Malaysia Incentive Postgraduate Grant, 1001/PKIMIA/821014. One of the authors (FY) would like to acknowledge Universiti Malaysia Terengganu, Malaysia for the study leave rendered.

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Scientific Research

Electrocatalytic Reduction of Oxygen at Perovskite (BSCF)-MWCNT Composite Electrodes

Farhanini Yusoff[1], Norita Mohamed[1], Azizan Aziz[2], Sulaiman Ab Ghani[1*]

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Received 13 December 2013; revised 19 January 2014; accepted 6 February 2014

Abstract

A composite paste electrode based on $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF)—initially synthesized by sol-gel method—and multiwall carbon nanotube (MWCNT) as a cathode in fuel cells is developed. The composite pastes are prepared by the direct mixing of BSCF:MWCNT at 90:10, 80:20 and 70:30 (% w/W). These electrodes are then characterized by the x-ray diffraction (XRD), scanning electron microscopy (SEM), nitrogen adsorption-desorption isotherm, electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV). The XRD and SEM confirm the inclusion and the uniform dispersal of the MWCNT within BSCF, respectively. The nitrogen adsorption isotherm study shows that the porosity of the composite paste electrode has been improved by two-fold from the BSCF electrode. The EIS and CV demonstrate that the higher ratios of MWCNT in the composites are critical in improving the electronic conductivity as well as the kinetics. It is also noticeable that the electrode has increased the catalysis of oxygen in 0.1 M KOH (pH 12.0). Cyclic voltammetric studies on the oxygen reduction reaction (ORR) suggest that the incorporation of MWCNT is vital in improving the electrode (cathode) properties of a fuel cell.

Keywords

$Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF); Catalysis; Composites; Multiwall Carbon Nanotube (MWCNT); Oxygen Reduction Reaction

1. Introduction

Although the oxygen reduction reaction (ORR) is important in variety of electrochemical processes including corrosion inhibition and metal-air batteries, the application of the ORR in fuel cells is of particular interest

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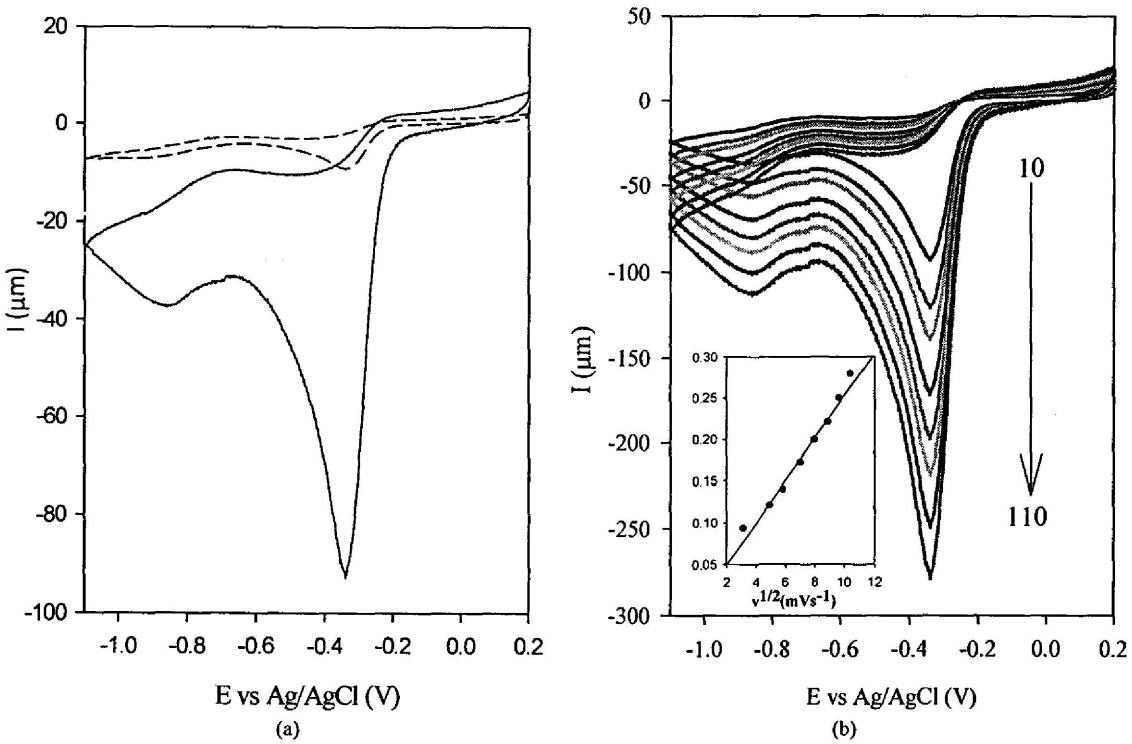

Figure 8. (a) CV of BSCF-MWCNT 70:30 with absence (dotted line) and presence (solid line) of O_2 in 0.1 M KOH and (b) CV scans of BSCF-MWCNT 70:30 at pH 12 recorded at different scan rates (Inset: linear relationship in peak current vs. the square root of the scan rate).

detached from the BSCF-MWCNT electrode.

4. Conclusion

A simple BSCF-MWCNT electrode has been prepared and optimized for ORR at pH 12. It has exhibited an excellent electrocatalytic activity towards ORR at the room temperature. The higher ratio of MWCNT in the composites is vital for better electrocatalysis. The MWCNT, the modifier material, has improved the performance of the BSCF on its charge-transfer, conductivity, oxygen adsorption and reduction. The application of BSCF-MWCNT electrode as a cathode for ORR in a fuel cell is then proposed. This is the subject for the next report.

Acknowledgements

This work was supported by the Ministry of Higher Education (MHE) Fundamental Research Grant Scheme (FRGS) No. 203/PKIMIA/6711263 and Universiti Sains Malaysia Incentive Postgraduate Grant, 1001/PKIMIA/821014. One of the authors (FY) would like to thank Universiti Malaysia Terengganu, Malaysia for the study leave rendered.

References

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